学校编码：10384　　密级_____

学号：20720101150117

厦门大学

硕　士　学　位　论　文

聚合物微球水热形貌调控及表面功能化

Hydrothermal morphological control of polymer microspheres and surface functionalization

张龙

指导教师姓名：　戴李宗 教授

专　业　名　称：　高分子化学与物理

论文提交日期：　2013年 5 月

论文答辩日期：　2013年 6 月

2013 年 6 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为(　　)课题(组)的研究成果，获得（　　）课题（组）经费或实验室的资助，在（　　）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　　）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　　月　　日

摘 要

α-Fe_2O_3纳米材料作为一类优越的半导体、软磁性材料，其合成及性能研究已成为近年来纳米材料领域的一个研究热点。纳米材料的形貌和尺寸往往对其性能有着决定性的影响。因此，α-Fe_2O_3纳米结构的可控制备一直以来都是一个具有挑战性的难题而备受材料科学家们的广泛关注。在众多合成方法中，水热法因易实现产物晶形、颗粒分散度、形貌和粒径的控制而备受青睐，形貌和功能各异的α-Fe_2O_3纳米材料已经通过水热法成功制备。具有高温、高压特征的水热法虽然在无机纳米材料的合成中被广泛采用，却极少应用于高分子纳米材料可控构筑领域。本文创新性地将聚合物微球与水热法结合，研究聚合物微球经水热处理后形貌和尺寸变化并通过在聚合物微球基体表面构筑纳米α-Fe_2O_3晶体来实现聚合物微球的表面功能化。具体研究工作如下：

（一）采用分散聚合、沉淀聚合、无皂乳液聚合制备三种单分散聚合物微球，分别为聚苯乙烯微米球、表面修饰聚乙二醇(PEG)的聚苯乙烯纳米微球、聚(苯乙烯-甲基丙烯酸羟乙酯)共聚纳米微球。探讨了引发剂用量、稳定剂用量、PEG链长、交联剂对微球尺寸和单分散性的影响。

（二）选用聚苯乙烯微米球和表面修饰PEG的聚苯乙烯纳米微球进行水热处理，研究其形貌和粒径的变化过程。探讨了透析、稳定剂浓度、PEG、离子浓度和温度对微球水热处理后产物形貌的影响，采用扫描电镜(SEM)、透射电镜(TEM)和动态光散射(DLS)表征微球水热处理后产物尺寸和单分散性的变化。

（三）选用表面修饰PEG的单分散聚苯乙烯纳米微球为模板，单一亚铁盐为铁源，采用水热法合成聚苯乙烯/α-Fe_2O_3微纳米二级结构。探讨了铁源用量/聚苯乙烯纳米微球质量比、PEG链长、交联聚苯乙烯纳米微球、亚铁盐阴离子种类对聚苯乙烯/α-Fe_2O_3微纳米二级结构形貌的影响。采用红外光谱(FTIR)、紫外-可见光谱(UV-vis)、X射线衍射(XRD)、扫描电镜(SEM)和透射电镜(TEM)表征聚苯乙烯/α-Fe_2O_3微纳米二级结构的组成、结构和形貌。通过研究反应组分的作用、水热前驱体溶液的组分和跟踪水热反应过程对聚苯乙烯/α-Fe_2O_3微纳米二级结构的合成机理进行了相关讨论和分析，并提出相关的合成机理模型。此外，还研究了

聚苯乙烯/α-Fe_2O_3微纳米二级结构对刚果红的吸附脱色性能，探索其作为水处理剂在污水处理领域的应用。

关键词： 聚合物微球 水热处理 α-Fe_2O_3 水热合成

Abstract

As a superior semiconductor and paramagnetic material, the synthesis and properties of nano α-Fe_2O_3 have become a hot research topic in recent years in the field of nanomaterials. Since the properties of nanomaterials are highly dependent on their morphology and size, controlling these factors for nanoscale α-Fe_2O_3 is of great importance and challenge to researchers. Among its multiple synthetic methods, hydrothermal synthesis was most popular because of its facility to control the crystal form, particle dispersion, morphology and particle size of the product. Various morphology and function of α-Fe_2O_3 nanostructures have been successfully prepared with the hydrothermal method. The hydrothermal method was frequently adopted in the synthesis of inorganic nanomaterial but was seldom applied to the field of polymer due to its characteristic high temperature and high pressure. This thesis combines polymer microspheres with the hydrothermal method. It was studied that polymer microspheres changed in morphology and size after hydrothermal treatment and the accurate fabrication of nano α-Fe_2O_3 on a polymer microsphere substrate achieved functionalization .The main contents are listed:

(1) Three kinds of monodispersed polymer microspheres: polystyrene(PS) micro-spheres, PS nanospheres with surfaces modified by PEG , and P(St-HEMA) nanospheres which were prepared by dispersion polymerization, precipitation polymerization, and soap-free polymerization. The size and monodispersity of the polymer microspheres could be particularly controlled by altering a variety of synthetic conditions, such as the dosage of initiator, stabilizer, chain length of PEG , or cross-linking agent.

(2) PS microspheres and PS nanospheres with surfaces modified by PEG, prepared by our previous work, were employed to study the change of polymer microspheres in morphology and particle size after hydrothermal treatment. The factors related to the resultant of the product such as dialysis, stabilizer , PEG ,ion concentration, temperature were also investigated. The change of the size and

monodispersity of resultant product was characterized through the use of a scanning electron microscopy (SEM), transmission electron microscopy(TEM), and dynamic Light Scattering(DLS).

(3) PS nanospheres with surfaces modified by PEG were adopted as templates to prepare PS/α-Fe_2O_3 with micro/nano hierarchical structures through the hydrothermal method. The factors related to the morphology of PS/α-Fe_2O_3 microspheres are the quality ratio of ferrite salt to PS microspheres, chain length of PEG, crosslinked PS microspheres, temperature and variety of the iron source anion. The PS/α-Fe_2O_3 microspheres with micro/nano hierarchical structures were characterized through the use of the Fourier transform infrared (FTIR), UV-visible spectroscopy, X-ray diffraction(XRD),Scanning electron microscopy(SEM), and Transmission electron microscopy(TEM). The reaction mechanism of PS/α-Fe_2O_3 with micro/nano hierarchical structures was also discussed and verified in detail through studying the action of the reagents, compostion of the precursor solution, and tracing of the reaction process and the relevant model was proposed. The absorbing and bleaching performance of of PS/α-Fe_2O_3 micro/nano hierarchical structure was investigated to explore its application as a water treatment agent in sewage treatment.

Keywords: Polymer microspheres; hydrothermal treatment; α-Fe_2O_3; hydrothermal synthesis；

目 录

摘 要.....I

Abstract.....III

第一章 绪论.....1

1.1 单分散聚合物微球.....1

1.1.1 单分散聚合物微球的定义和应用.....1

1.1.2 单分散聚合物微球的合成方法简介.....2

1.2 α-Fe_2O_3 纳米材料.....4

1.2.1 α-Fe_2O_3 纳米材料的制备方法简介.....4

1.2.2 α-Fe_2O_3 纳米材料的特性.....12

1.3 聚苯乙烯/无机粒子复合微球.....14

1.3.1 聚苯乙烯/无机粒子复合微球的概述.....14

1.3.2 聚苯乙烯/无机粒子复合微球的制备方法.....14

1.3.3 聚苯乙烯/无机粒子复合微球的应用.....18

1.4 本论文的设计思想及主要内容.....18

参 考 文 献.....19

第二章 单分散聚合物微球的合成与表征.....30

2.1 引言.....30

2.2 实验部分.....31

2.2.1 实验试剂及仪器.....31

2.2.2 单分散聚苯乙烯微球的制备.....32

2.2.3 表征与测试.....33

2.3 结果与讨论.....34

2.3.1 分散聚合制备单分散聚苯乙烯微米球.....34

2.3.2 沉淀聚合制备表面修饰聚乙二醇的单分散聚苯乙烯纳米微球.....36

2.3.3 无皂乳液共聚制备单分散聚(苯乙烯-甲基丙烯酸羟乙酯)纳米微球.....40

2.4 本章小结.....42

参 考 文 献 43

第三章 聚苯乙烯微球的水热形貌调控 45

3.1 前言 45

3.2 实验部分 45

3.2.1 实验原料 45

3.2.2 聚苯乙烯微球水热处理实验 46

3.2.3 表征与测试 47

3.3 结果与讨论 47

3.3.1 聚苯乙烯微米球水热反应的影响因素探究 47

3.3.2 表面修饰聚乙二醇的聚苯乙烯纳米微球水热反应的影响因素探究 52

3.3.3 聚苯乙烯微米球水热过程研究 54

3.3.4 表面修饰聚乙二醇的聚苯乙烯纳米微球水热过程研究 55

3.4 本章小结 56

参考文献 57

第四章 聚苯乙烯/α-Fe_2O_3 微纳米二级结构的水热合成及其对刚果红吸附脱色性能的研究 58

4.1 引言 58

4.2 实验部分 59

4.2.1 实验试剂及仪器 59

4.2.2 聚苯乙烯/α-Fe_2O_3 微纳米二级结构的水热合成 60

4.2.3 探索合成机理的相关实验 61

4.2.4 刚果红吸附脱色实验 61

4.2.5 表征与测试 61

4.3 结果与讨论 62

4.3.1 形貌可控的聚苯乙烯/α-Fe_2O_3 微纳米二级结构 62

4.3.2 聚苯乙烯/α-Fe_2O_3 微纳米二级结构的表征 67

4.3.3 聚苯乙烯/α-Fe_2O_3 微纳米二级结构的合成机理研究 72

4.3.4 聚苯乙烯/α-Fe_2O_3 微纳米二级结构对刚果红吸附脱色性能研究 79

4.4 本章小结 80

参 考 文 献 80

第五章 全文结论 84

硕士期间发表的论文与专利 87

致 谢.....88

Table of Contents

Abstract in Chinese ..... **I**

Abstract in English ..... **III**

1 Introduction **1**

1.1 Monodisperse polymer microspheres **1**

1.1.1 Definition & application of monodispersed polymer microspheres 1

1.1.2 Synthesis of monodispersed polymer microspheres 2

1.2 α-Fe_2O_3 nanomaterial **4**

1.2.1 Synthesis of α-Fe_2O_3 nanomaterial 4

1.2.2 Character of α-Fe_2O_3 nanomaterial 12

1.3 PS/inorganic particle composite microspheres **14**

1.3.1 Overview of PS/inorganic particle composite microspheres 14

1.3.2 Synthesis of PS/inorganic particle composite microspheres 14

1.3.3 Application of PS/inorganic particle composite microspheres 18

1.4 Content and purposes on the thesis **18**

References **19**

2 Synthesis and characterization of monodispersed polymer microspheres **30**

2.1 Introduction **30**

2.2 Experimental **31**

2.2.1 Reagents and instruments 31

2.2.2 Synthesis of monodispersed PS microspheres 32

2.2.3 Characterization and Measurement 33

2.3 Results and discussion **34**

2.3.1 Monodispersed PS micro-spheres 34

2.3.2 Monodispersed PS nano-pheres with surface modificated by PEG 36

2.3.3 Mondispersed P(St-HEMA) nano-spheres 40

2.4 The Conclusion of this Chapter....42

References....43

3 Hydrothermal morphology control of PS microspheres....45

3.1 Introduction....45

3.2 Experimental....45

3.2.1 Reagents....45

3.2.2 Hydrothermal treatment of PS microspheres....46

3.2.3 Characterization and Measurement....47

3.3 Results and discussion....47

3.3.1 Influencing factor of PS micro-spheres under hydrothermal treatment....47

3.3.2 Influencing factor of PS nano-spheres with surface modificated by PEG under hydrothermal treatment....52

3.3.3 Research of hydrothermal process of PS micro-spheres....54

3.3.4 Research of hydrothermal process of PS nano-spheres with surface modificated by PEG....55

3.4 The conclusion of this chapter....56

References....57

4 Hydrothermal synthesis and functional research of PS/α-Fe_2O_3 micro/nano dual structure....58

4.1 Introduction....58

4.2 Experimental....59

4.2.1 Reagents and instruments....59

4.2.2 Hydrothermal synthesis of PS/α-Fe_2O_3 micro/nano dual structure....60

4.2.3 Experiment related with Mechanism....61

4.2.4 Congo red decolorization adsorption experiment....61

4.2.5 Characterization and Measurement....61

4.3 Results and discussion....62

4.3.1 Controllable morphology of PS/α-Fe_2O_3 micro/nano dual structure....62

4.3.2 Characterization of PS/α-Fe_2O_3 micro/nano dual structure....67

4.3.3 Synthesis Mechanism of PS/α-Fe_2O_3 micro/nano dual structure....72

4.3.4 Adsorption performance of PS/α-Fe_2O_3 micro/nano dual structure....79

4.4 The conclusion of this chapter 80

References 80

5 Conclusion 84

Published Patents and Papers During Postgraduate 87

Acknowledgement 88